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Technical Paper 146

DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, SECRETARY
BUREAU OF MINES
VAN. H. MANNING, DIRECTOR

THE NITRATION OF TOLUENE

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no. 146
ENGINEERING

BY

E. J. HOFFMAN

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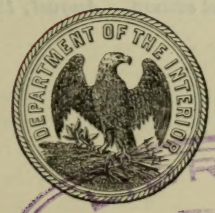

RARY
JUN 25 1917
UNIVERSITY OF TORONTO.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1916

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First edition. August, 1916.

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THE NITRATION OF TOLUENE.

By E. J. Hoffman.

INTRODUCTION.

This paper is the result of experiments made in the Bureau of Mines on the preparation of trinitrotoluene from toluene obtained in the manufacture of water gas. There seems to be a rather prevalent view that so-called water-gas toluene is unsuitable for the manufacture of trinitrotoluene, because of the toluene containing hydrocarbons of the aliphatic series whose removal can not be effected by the usual methods of purification. It was in anticipation of such difficulty that the present investigation was undertaken.

The investigation early showed that if the sample of water-gas toluene under investigation contained any aliphatic hydrocarbons they were present in negligible quantity so far as affecting nitration. Consequently, the investigation became a more general one, embracing the nitration of any good grade of toluene, and it was continued with a view not only of ascertaining the conditions under which the best yield of trinitrotoluene could be obtained from the sample in hand, but also of developing a method that might be capable of satisfactory industrial application to the nitration of any toluene of approximately the same degree of purity.

Ample justification for such an investigation is to be found in the incompleteness of published details with respect to methods already successfully applied in the industries. Although much valuable information was available in the literature on the nitration of toluene, the author was unable to select any method or combination of methods described that could be said to cover the whole problem in hand; nor were the data available sufficient to determine the relative merits of different procedures with respect to quantity and quality of yield of trinitrotoluene.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to Prof. C. E. Munroe and to Prof. G. A. Hulett, consulting chemists, of the Bureau of Mines, for the interest they have shown in the progress of the work, which was suggested by Prof. Munroe.

The investigation was undertaken with the active cooperation of C. G. Storm, formerly explosives chemist of the bureau, to whom

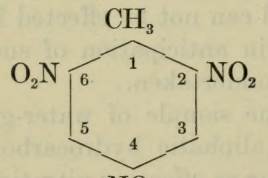
the author is indebted for results of earlier experiments as well as for helpful suggestions in the course of the investigation.

The toluene used in this investigation was supplied by Mr. Paul Thompson, fifth vice president of the United Gas Improvement Co., whose kindness the author hereby acknowledges.

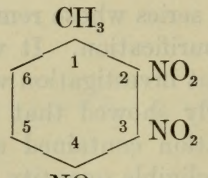
The author desires also to express his appreciation of the valuable suggestions and assistance rendered from time to time by W. C. Cope, explosives chemist, J. E. Crawshaw, junior chemist, and J. H. Hunter, formerly junior chemist, of the bureau's staff.

THEORY OF TOLUENE NITRATION.

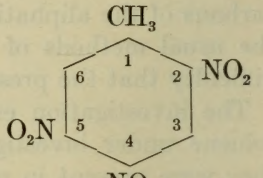
Of the six isomeric trinitrotoluenes theoretically possible, only three have been prepared directly by the nitration of toluene, as follows:



α or 2–4–6 trinitrotoluene (melting point, 80.6° C.). (41, 47, 52, 56; compare 58.)

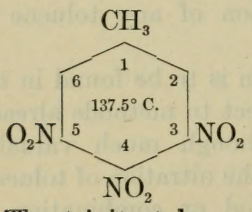


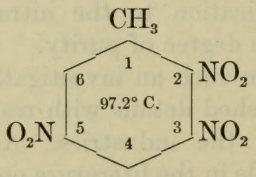
β or 2–3–4 trinitrotoluene (melting point, 112° C.). (15, 52, 56.)

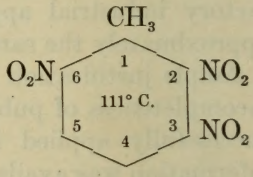


γ or 2–4–5 trinitrotoluene (melting point, 104° C.). (15, 52, 56.)

Recently, however, Koerner and Contardi (54; see also 56) have prepared by indirect methods the three remaining isomers:







The trinitrotoluene used as an explosive is the α or symmetrical (2–4–6) trinitrotoluene, and this isomer mainly is obtained by the direct nitration of toluene either in one operation or through successive operations involving the formation of the various mononitrotoluenes and dinitrotoluenes as intermediate products.

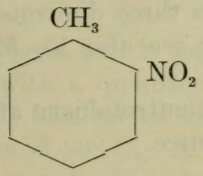
Pure symmetrical trinitrotoluene forms small white crystals which on exposure to the light assume a pale-yellow to brown color. The compound is completely soluble in ether, acetone, benzene, toluene, ligroin, or hot ethyl alcohol; slightly soluble in cold alcohol, and very slightly soluble in cold or hot water. It is neutral and forms no salts with metals. Its melting point is 80.6° C.; melted and solidified, it has a density of 1.54 to 1.57, which by pressure and rapid cooling may be increased to 1.61 (47). It is a highly stable substance, is insensitive to blows, burns rapidly without detonation,

and is exploded by the use of a strong mercury fulminate cap. Hence its manufacture is comparatively safe.

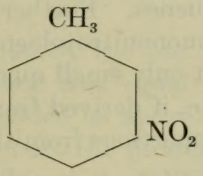
Except for differences in melting points, the β and γ trinitrotoluenes do not differ essentially in physical properties from the α trinitrotoluene (52).

The products resulting from the nitration of toluene are dependent on the conditions under which the operation is conducted. Among such conditions are quantity and concentration of acid or acids used and temperature of nitration. These various mononitrotoluenes, dinitrotoluenes, and trinitrotoluenes have been the subject of many experimental investigations, and the theoretical problem of their production may be considered largely solved. The successive stages of nitration may be indicated as follows:

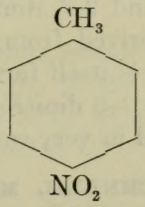
1. Nitration of toluene to its isomeric mononitro derivatives:



o nitrotoluene (boiling point, 218° C.). (25; compare 21.)



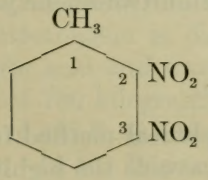
m nitrotoluene (boiling point, 228° C.). (14.)



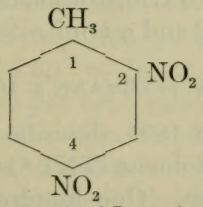
p nitrotoluene (melting point, 54° C.) (6, 21, 27; compare 58); (boiling point, 238° C.) (16; compare 21, 27).

The proportions of the ortho and para compounds formed appear to be influenced by the temperature of nitration (27, 33, 34, 39). The meta compound is formed only in small amounts, usually 1 to 2 per cent; the maximum proportion reported is 4 per cent (39).

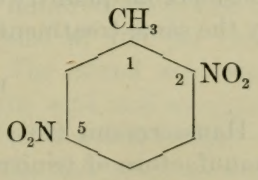
2. Further nitration of the mononitrotoluene mixture yields the six theoretically possible isomeric dinitrotoluenes:



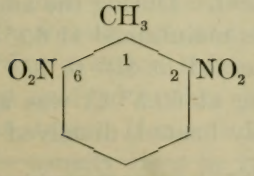
Melting point, 63° C. (29, 52).



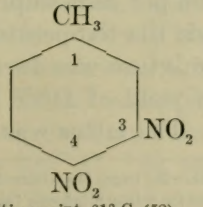
Melting point, 71° C. (24, 52; compare 30, 58).



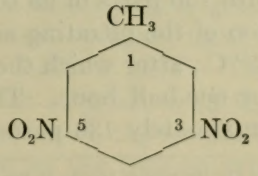
Melting point, 52° C. (52).



Melting point, 66° C. (31, 52; compare 18).



Melting point, 61° C. (52).



Melting point, 92° C. (28, 52).

The 2–4 and 2–6 dinitrotoluenes are present in the resulting mixture in by far the largest proportions.

3. Further action of nitrating acids on the dinitrotoluenes gives the following trinitro compounds (52):

2–4 dinitrotoluene yields	2–4–6 trinitrotoluene (α)
2–6 dinitrotoluene yields	2–4–6 trinitrotoluene (α)
2–3 dinitrotoluene yields	2–3–4 trinitrotoluene (β)
2–5 dinitrotoluene yields	2–4–5 trinitrotoluene (γ)
3–4 dinitrotoluene yields	2–3–4 trinitrotoluene (β) and 2–4–5 trinitrotoluene (γ)

3–5 dinitrotoluene is not further acted upon.

Of the three isomeric trinitrotoluenes thus indicated in the final products of nitration the formation of the β and γ isomers in any considerable amounts is not to be expected. In the first place, it is to be noted that β and γ trinitrotoluenes are formed from the 2–3, 3–4, and 2–5 dinitrotoluenes. Further, these three dinitrotoluenes are derived from metamononitrotoluene (38; see also 15, 52, 53), which is itself formed in only small quantity.

The 2–5 dinitrotoluene, if derived from orthonitrotoluene at all, is formed in very small proportions from that source.

TECHNICAL METHODS FOR MANUFACTURE OF TRINITROTOLUENE.

EARLY PROCESSES.

A trinitrotoluene having a melting point of 82° C. was prepared in 1863 by Wilbrand (5) by the action of fuming nitric and sulphuric acids on toluene. By the further nitration of dinitrotoluene, Beilstein and Kuhlberg (9), in 1870, and Tiemann (10), in 1870, obtained similar products. In 1882 Hepp (15), by the action of very concentrated acids on paranitrotoluene and 2–4 dinitrotoluene, obtained a considerable quantity of α trinitrotoluene. Metanitrotoluene yielded by the same treatment β and γ trinitrotoluene.

HÄUSSERMANN'S METHOD.

Häussermann (26), in 1891, described a technical method for the manufacture of trinitrotoluene (TNT [a]) which avoids the highly concentrated acids of Hepp. One hundred parts of paranitrotoluene was treated with a mixture of 75 parts of 91 to 92 per cent nitric acid with 150 parts of 95 to 96 per cent sulphuric acid. During the addition of the nitrating acids the temperature was maintained at 60° to 65° C., after which the mixture was further heated at 80° to 85° C. for one-half hour. The yield of DNT melting at 69.5° C. was approximately 130 parts. The latter was slightly heated, dissolved in

[a] For the sake of brevity in the following pages the abbreviation "TNT" is used for "trinitrotoluene." Similarly "DNT" and "MNT" stand for "dinitrotoluene" and "mononitrotoluene."

4 parts of 95 to 96 per cent sulphuric acid, and treated with 1.5 parts of 90 to 92 per cent nitric acid, after which the temperature was kept at 90° to 95° for 4 to 5 hours. The yield of TNT (melting point 79° C.) was 105 parts from 100 parts of DNT. By recrystallization a product having a melting point of 81.5° C. was obtained.

METHOD OF VASQUEZ.

Vasquez (42), in 1911, described a method for the manufacture of TNT from toluene in three stages, and gave details of apparatus and procedure in manufacture and refining. According to this method the spent acids (90 liters) from the preparation of DNT are fortified with the required nitric acid and added to an equal weight of toluene, with constant stirring and with cooling, to prevent a rise of temperature above 30° C. After standing 6 hours the resultant MNT is separated.

The spent acid is regenerated by the use of sulphur trioxide and mixed with a quantity of nitric acid equal in weight to the MNT formed. The mixed acid is added as above to the MNT at a temperature of 90° C. After 6 hours the product is cooled to −2° C., and the spent acid is drawn off from the DNT.

For the third stage of nitration stronger acids are added to the molten DNT, raising the temperature to 92° C. After 20 hours the mixture is transferred to another vessel, and after 4 to 5 days the separated sclid is washed with water and alkali, then refined by being washed with acetone and soda, and finally crystallized from alcohol.

LANGENSCHEIDT'S METHOD.

A method devised by Langenscheidt (45) to obviate the necessity of separating the DNT from the spent acid after the conversion of orthonitrotoluene into DNT is as follows: Five hundred kilograms of orthonitrotoluene is dissolved in 1,400 kilograms of 100 per cent sulphuric acid and warmed to 60° to 70° C. The mixed acid consisting of 700 kilograms of 100 per cent sulphuric acid and an equal weight of 48° B. (94.09 per cent) acid is introduced in a thin unbroken stream. In the beginning the reaction is violent, and much cooling is required; as the nitration proceeds the heat evolved decreases. A fall in temperature indicates that the orthonitrotoluene has gone over into the second stage of nitration. All the mixed acid is gradually introduced, and the whole is slowly warmed up again until a further reaction takes place—the nitration of DNT to TNT. The heat evolved in this stage of the nitration is not so great as in the first stage. If means of cooling the liquid are not used, the temperature usually rises to 120° to 130° C. As soon as the temperature begins to fall the contents of the nitrating vessel are brought to 150° C.,

and this temperature, or, just as well, a temperature of 120° to 130° C., is maintained for about one hour. When the reaction mixture has cooled to 100° C., about 200 liters of water is added to increase the yield.

Langenscheidt's method for manufacturing TNT from DNT is as follows: Five hundred kilograms of DNT is placed in the apparatus and melted; the mixed acid consisting of 1,125 kilograms of oleum (20 per cent) and 305 kilograms of nitric acid (48° B.) is slowly added at 70° to 75° C. When the addition of acid has been completed, the contents of the apparatus are slowly and carefully warmed. The reaction begins at 90° to 100° C., and a temperature of 130° C. is reached, which is maintained for one hour, after which the products are cooled to 100° C. and treated as above with water.

The resultant TNT separated cold by the method here indicated, or in the liquid condition, is forced into lead wash tanks containing water at 40° to 45° C., and washed with steam till neutral. By crystallization from a mixture of 9 parts of alcohol and 1 part of benzene a product is obtained that melts at 81° to 82° C. and solidifies at 80.3° to 80.4° C.

METHOD OF VENNIN AND CHESNEAU.

The following method of Vennin and Chesneau (49) provides for the direct nitration of toluene to TNT in one operation: Twenty kilograms of toluene is added slowly to a mixture of 80 kilograms of 91 to 92 per cent nitric acid, 450 kilograms of 93 to 94 per cent sulphuric acid, and 25 kilograms of oleum (60 per cent sulphur trioxide) at 40° C. The mixture is then heated 2 hours at 80° to 85° C. and 3 hours at 100° to 105° C. After the mixture has cooled the spent acids are drawn off, and the TNT is crystallized from hot sulphuric acid and washed with hot water. The product thus obtained melts at 77° to 79° C. By washing with 95 per cent alcohol, or alcohol containing 10 per cent benzene, a product is obtained that melts at 81° C. The yield is given as 150 per cent referred to the toluene used.

IMPORTANCE OF AVAILABLE ALCOHOL.

As prepared by the methods described above the TNT of desired purity is obtained by crystallization from alcohol. If the necessary alcohol is available at a reasonable cost this procedure presents no difficulties, but if, for economic reasons, alcohol can not be used it is necessary to proceed in such a way that crystallization of the water-washed product is avoided. The direct nitration of toluene to dinitrotoluene yields mainly the 2–4 DNT; but the product contains also 7 to 10 per cent of an orange-yellow oil known as "drip oil" (German

"Tropföl" or "Binitropföl"), which investigation (11, 12, 16, 17, 19, 28, 30, 50, 53) has shown to consist of traces of orthonitrotoluene, about equal parts of meta and para MNT, the 2–4, 2–5, 2–6, and 3–4 DNT's, 2–4–6 TNT, and either 2–3–5 or 2–3–6 TNT. In Germany this liquid affords a valuable and economical starting point in the manufacture of TNT. In Italy, however, by starting with a DNT product having a melting point of 63° to 66° C., a TNT is prepared that without crystallization from alcohol melts at a temperature only 1° to 1.5° lower than that required for the pure TNT.

GIUA'S METHOD.

Giua (56) recently describes a method for thus preparing a high grade of TNT. Pure toluene, in a special nitration apparatus provided with a stirring device to keep the liquid constantly agitated, is nitrated with a mixture of nitric and sulphuric acids containing 18 to 22 per cent nitric acid and 15 to 20 per cent water. To assure a satisfactory product, 1.5 to 1.8 times the theoretical amount of nitric acid must be used. The temperature of reaction must not rise above 110° to 120° C. By the use of the centrifuge or other mechanical means the drip oil formed can be removed sufficiently from the solid DNT so that by washing well with water a product is obtained that melts at 63° to 66° C.

Subsequent nitration of this product is accomplished by treatment with anhydrous acid containing 18 to 25 per cent nitric acid, the ratio of toluene to nitrating acid being 1 to 4 or 1 to 5. The reaction begins at 60° to 65° C.; the temperature is regulated by cooling means so that it does not exceed 118° to 122°. By treatment with the nitrating acid mentioned in the ratio of 1 to 2 the red oil removed from the solid DNT yields a 66° product.

METHOD OF ESCALES.

Escales (57) has described in detail apparatus and methods for preparing the various nitrotoluenes, the following abstract being taken from his description.

1. *Mononitrotoluene.*—The toluene (200 kilograms) is introduced into the proper nitrating vessel, provided with a cooling and a stirring apparatus. The nitrating acids, 350 kilograms of 66° B. sulphuric acid (specific gravity 1.84) and 225 kilograms of 44.1° B. nitric acid (specific gravity 1.41), are added over a period of 8 hours. The temperature attained in 1 hour (60° C.) must not be exceeded. After introduction of all the acid the operation is continued 2 hours longer, after which the mixture is allowed to stand overnight. The spent acid is used over again for the preparation of the next lot of MNT, after addition to it of 150 kilograms of 44.1° B. nitric acid. If the

mononitrotoluene is desired for other purposes, isomers may be separated and purified. Otherwise this crude mixture is further nitrated to DNT.

2. *Dinitrotoluene.*—To the crude MNT prepared in the manner described is added a stronger acid mixture, 675 kilograms of 66° B. sulphuric acid, and 225 kilograms of 46.8° B. nitric acid (specific gravity 1.445), over a period of 6 hours. In about 1.5 hours the temperature normally reaches 115° C. The operation is completed in a total time of 9 hours, when the DNT is separated hot from the acids and emptied into boiling water. If the course of the reaction has been defective the oil ("Binitropföl") thus formed is allowed to drain off. Otherwise the total product is crushed and treated with water. Any impure product present collects on the surface of the water and can be removed. In operations 1 and 2, 200 kilograms of toluene yields 350 to 360 kilograms of dry DNT, or 90 to 93 per cent of that required by theory.

3. By the use of still stronger acids the pure DNT may be readily converted into TNT.

The methods of Häussermann, Vasquez, and Langenscheidt are given in detail.

DESCRIPTION OF NITRATION EXPERIMENTS.

FOUR METHODS OF PREPARING TRINITROTOLUENE.

The methods outlined above for the preparation of trinitrotoluene involve all of the four possible procedures for converting toluene into the desired product, as follows:

1. A one-stage method, comprising the direct nitration of toluene to trinitrotoluene in one operation.

2. A two-stage method, comprising: (*a*) The conversion of toluene into dinitrotoluene; and (*b*) the further nitration of the dinitrotoluene to trinitrotoluene.

3. A two-stage method, comprising (*a*) the preparation of mononitrotoluene; and (*b*) the conversion of mononitrotoluene into trinitrotoluene.

4. A three-stage method, comprising: (*a*) The preparation of mononitrotoluene; (*b*) the conversion of mononitrotoluene into dinitrotoluene; (*c*) the further nitration of dinitrotoluene to trinitrotoluene.

METHOD 1.

A modification of the method described by Vennin and Chesneau was employed by the author of this paper in the nitration of a laboratory sample of toluene boiling at 110.5° C. Because of the low yield of TNT (138 grams—melting point 79.5° to 81° C.—per 100 grams of toluene) and the large amount of acid required, this method was abandoned as uneconomical.

METHOD 2.

No effort was made to utilize method 2 on account of the recognized difficulties due to the formation of liquid products ("drip oil") along with the solid dinitrotoluenes. Two preliminary experiments gave very unsatisfactory results.

METHODS 3 AND 4.

Probably method 4 is the one most commonly used by manufacturers of TNT, at least in this country, and in addition to any other economical advantages it may possess, it is much the most satisfactory if the manufacturer desires to utilize a part of the mononitrotoluene and dinitrotoluene products for purposes other than the preparation of TNT. But if it is desired to convert the toluene wholly into TNT and no regard is had to intermediate products, except in so far as these affect the quality and amount of the final product, method 3 seems to possess certain advantages. For the especial reason that method 3 eliminates the necessity of separation of the DNT mixture, the author selected it as most promising for investigation and development in connection with the nitration of the water-gas toluene. Method 4 was tried only by way of comparison with the procedure finally determined on the basis of method 3.

CHARACTER OF TOLUENE USED IN EXPERIMENTS.

RESULTS OF DISTILLATION.

A sample of the water-gas toluene (352.4 grams), dried over calcium chloride for two days, was distilled from a 700-c. c. flask provided with a Hempel still head 26.7 cm. in length. The results of distillation were as follows:

Results of distillation of water-gas toluene.

Temperature interval, corrected, °C.	Weight of distillate.	Distillate.
	Grams.	*Per cent.*
100 to 107.6	4.0	1.13
107.6 to 108.4	6.7	1.90
108.4 to 109.4	30.2	8.57
109.4 to 109.8	75.1	21.31
109.8 to 110.1	125.3	35.56
110.1	102.8	29.17
110.1	[a] 8.2	[a] 2.33
	352.3	99.97

[a] Remaining in still head.

The boiling point of pure toluene has been variously stated. Among the values given are the following: Landolt and Jahn,[a] 110° C.; Timmermans,[b] 110.7° C. ± 1; Neubeck,[c] 110.8° C.

[a] Landolt, H., and Jahn, Hans, Molekularfraktion, etc.: Ztschr. phys. Chem., Bd. 10, 1892, p. 292.

[b] Timmermans, J., Sur la purification et les constantes physiques de quelques liquides organiques: Bull. Soc. chim. Belg., t. 24, 1910, p. 265.

[c] Neubeck, F., Ueber Molekularvolumina aromatischer Verbindungen: Ztschr. phys. Chem., Bd. 1, 1887, p. 656.

A sample of the toluene as received, not dried, was distilled in a similar manner. The first 10 per cent of distillate (up to 108.4° C.) came over milky, indicating the presence of water.

DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity of the toluene was determined with a pycnometer. Duplicate determinations of the specific gravity of a sample of the toluene which had been dried over calcium chloride gave the values 0.8658 and 0.8660 at 20°/4° C.

The specific gravity at 20°/4° C. of the fraction of the toluene distilling at 110.1°C. (102.8-gram fraction mentioned under "Results of Distillation of Water-Gas Toluene," p. 13), determined in the same manner, was 0.8657.

According to Landolt and Jahn, the specific gravity of pure toluene at 20.4°/4° C. is 0.86542. Calculated from their formula:

$$d_4^t = 0.88418 - 0.00091961t$$

$$d_4^{20} = 0.8658.$$

FREEZING TESTS.

A sample of the toluene after standing over calcium chloride for one week was cooled in a test tube to −17° C. in an ice-salt cooling mixture. At this temperature there was a separation of a small quantity of white solid which when warmed again to −12° C. entirely disappeared. A sample of the fraction distillating at a temperature of 108.4° to 109.4° C. (see "Results of Distillation of Water-Gas Toluene," p. 13), behaved in the same manner. From the 110.1° distillate no such separation of solid occurred at −17° C.

One drop of pure benzene was added to a part of the 110.1° distillate. At −15° C. there was a separation of solid which melted again at −8° C. A drop of water added instead of the benzene to a part of the same distillate caused a separation of solid at −15° C., which persisted up to +5° C.

A sample of the original toluene dried over calcium chloride was cooled in a test tube by means of a mixture of acetone and solid carbon dioxide. At −65° C. the total solid material separated was estimated as amounting to less than 1 per cent of the sample. This melted completely at about −12° C. There was no apparent increase of solid material separated at −77.5° C. At −79.5 °C. less solid separated from the 110.1° fraction than from the dried toluene itself.

A sample of the dried toluene was cooled in a bath of gasoline cooled by means of liquid air. The whole solidified at −91° C. (uncorrected reading). It nearly all melted at −50° C. The freez-

ing point of toluene as determined by Guttmann [a] is −92.4° C. No identification of the approximately 1 per cent solid separating as low as −79.5° C. was attempted.

DIMETHYLSULPHATE AND SULPHONATION TESTS FOR PARAFFINS.

The well-known dimethylsulphate and sulphonation tests for paraffins both gave negative results, but those tests were scarcely to be relied on in this connection.

The distillation experiments, specific gravity determinations, freezing tests, and dimethylsulphate and sulphonation tests indicated a high degree of purity for the toluene. The presence of some water and probably also of benzene was indicated. Whether other impurities were present and, if so, their nature was not established. However, the tests showed that the total impurities did not exceed approximately 1 per cent, and that figure was borne out by nitration experiments later described.

PREPARATION OF MONONITROTOLUENE.

The first step in the nitration of toluene was performed in a simple apparatus consisting of an ordinary wide-mouth bottle, of approximately 1-liter capacity, provided with a glass stirrer propelled by a small motor, and placed within a larger glass vessel through which water of the required temperature was allowed to flow. Temperature readings were made by means of an ordinary thermometer. The nitrating acid was placed in the bottle and the toluene was introduced slowly, with constant stirring of the acid mixture, or the reverse procedure of adding the acid to the toluene was followed.

The details of two experiments designated "Procedure A" and "Procedure B," are given below as illustrating the method and indicating the character and yield of the product:

PROCEDURE A.

To 200 grams of toluene cooled to 9° C. by ice water in the cooling vessel a mixture of 587 grams of sulphuric acid of 1.84 specific gravity and 293.5 grams of nitric acid of 1.42 specific gravity (50 per cent in excess of theoretical nitric acid) was slowly added from a dropping funnel, with constant stirring of the contents of the bottle. The addition of the acid and the cooling of the reacting mixture were so regulated that a temperature of 20° to 30° C. was maintained during the greater part of the operation. Owing to loss of control the temperature was as high as 30° to 50° C. for a few minutes in the early part of the operation. The time consumed in completing the intro-

[a] Guttmann, L. F., The determination of melting points at low temperatures: Jour. Chem. Soc., vol. 87, 1905, p. 1042.

duction of the acid was 1 hour and 20 minutes. Afterwards the water in the cooling vessel was run out and the stirring continued one-half hour longer. After standing over night in a separatory funnel, the spent acid and the nitration product, a clear light-yellow liquid, were separated. The yield of crude MNT as thus separated was 320 grams.

Eighty grams of this crude product, corresponding to the yield from 50 grams of toluene, was carefully washed with water till free from acid, dried over calcium chloride for several days, filtered, and weighed. The acid washings were made slightly alkaline with sodium hydroxide, and were extracted with ether. The ether solution dried over calcium chloride was used for extracting the MNT adhering to the flask and in the chloride used in drying the other larger fraction of the product. The total weight of MNT thus obtained was 71.5 grams. This product had a specific gravity of 1.1818 at 22° C. and a nitrogen content of 10.58 per cent. Pure MNT contains 10.22 per cent nitrogen, and crude MNT, according to Escales, has a specific gravity of approximately 1.165. Fifty grams of pure toluene yields theoretically 74.46 grams of MNT.

For further nitration the crude unwashed product was used, so that no losses due to purification had to be considered.

PROCEDURE B.

In the second experiment the same weights of toluene and acids were used as in the first, but the toluene was added to the acids. Otherwise the procedure was the same. Little difficulty was experienced in maintaining a temperature of 13° to 30° C. during the operation of mixing, which lasted two hours. As before, the stirring was continued one-half hour after the mixing had been completed. The yield of crude product was 331.4 grams. Purified as above, 248.55 grams yielded 243.4 grams, having a specific gravity of 1.2450 and a nitrogen content of 12.14 per cent.

The high values for specific gravity and nitrogen were due to the formation of considerable dinitrotoluene, as the following data regarding the product show:

Results of distillation of 111.8 grams of crude mononitrotoluene at a pressure of 30 mm.

Fraction.	Temperature interval.	Weight of fraction.	Fraction.
	° C.	*Grams.*	*Per cent.*
A	115 to 160	68.1	60.91
B	162 to 185	40.7	36.41
Residue		2.5	2.68
Loss		0.5	

Fraction A was a liquid having a specific gravity of 1.1750 and a nitrogen content of 10.34 per cent, or practically pure MNT, which contains 10.22 per cent nitrogen.

Fraction B was a white solid mass containing 15.13 per cent nitrogen, or nearly pure DNT, which contains 15.38 per cent nitrogen.

Calculated from the data of the nitrogen determination of the purified products before distillation, the values of 62.93 per cent and 37.07 per cent are obtained for the mononitrotoluene and dinitrotoluene contents, respectively, which are in close accord with the distillation values. These calculations are necessarily based on the assumption that only MNT and DNT were present.

A further simple calculation is as follows: One hundred grams of toluene yielded 162.26 grams of purified product, or 102.11 grams of MNT (62.93 per cent) and 60.15 grams of DNT (37.07 per cent). The latter quantity of DNT corresponds to 45.28 grams of MNT. Hence the 100 grams of toluene yielded a total of 147.39 grams of MNT which in turn corresponds to 98.98 grams of toluene.

In view of the above results it is evident that Procedure B can not be followed if the nonformation of dinitrotoluene is desired. In that case, of the two procedures, Procedure A must be followed instead. Other experiments indicated, however, that Procedure B may be used with little formation of DNT, provided the excess of nitric acid over the theoretical amount required for the nitration is small. But under such conditions some of the toluene will escape nitration; the product obtained in one experiment in which an excess of 25 per cent nitric acid was employed had a strong odor of toluene. In the use of less than 40 to 50 per cent excess nitric acid in Procedure B, the further difficulty of maintaining the progress of the reaction and also of avoiding the formation of very dark reaction mixtures, often of dark sludge, resulting frequently in the impossibility of separating the product from the spent acid, is to be ascribed to the depletion of the nitric acid by the formation of DNT. With 50 per cent excess nitric acid, however, no such difficulty was experienced, and if the temperature of reaction was not allowed to exceed 50° C., the resultant product was a clear yellow liquid from which the spent acid was readily drawn. If, on the other hand, a greater excess of nitric acid than 50 per cent is employed for nitration, the proportion of DNT formed may be large enough to result in its separation from solution in the liquid MNT, with consequent difficulty in effecting a separation of the product from the spent acid, and in the possible difficulties encountered when TNT is prepared from DNT. In one experiment 50 grams of toluene treated with an acid mixture containing 100 per cent excess nitric acid yielded 90 grams of a crude product which was almost entirely solid DNT.

Inasmuch as the resultant crude product designated as MNT is to be used for the preparation of TNT, the formation of DNT is of much less consequence than is the loss of toluene, and besides some 40 per cent of the 50 per cent excess nitric acid is used up in converting

a part of the MNT into DNT. For these reasons and because the temperature of nitration was easier to control than in Procedure A, Procedure B was followed in the preparation of the MNT in most of the experiments. In general, effort was made to keep the temperature of reaction below 30° C., and no subsequent heating was required. But the experiments did not show that a temperature as high as 50° C. either decreased the yield or affected seriously the character of the product.

Table 1 following gives data regardin the experiments upon which the above conclusions are based:

TABLE 1.—*Data regarding experiments covering preparation of mononitrotoluene from toluene.*

Experiment No.	Weight of toluene.	Per cent of nitric acid in excess of theoretical.	Ratio of nitric acid to sulphuric acid.	Temperature of mixing.	Time of mixing.	Subsequent heating.	Yield of crude MNT.	Yield of acid-free and dry MNT.	Specific gravity of acid-free and dry MNT.	Per cent of nitrogen.	Remarks.
	Grams.			*° C.*	*Minutes.*		*Grams.*	*Grams.*			
1	50	10	1 : 2	20 to 30	30	1½ hours at 90° to 95° C	72.0				
2	50	10	1 : 3	25 to 35	35	1 hour up to 95° C.; 2 hours at 95° to 97° C.					Dark-green mixture; no separation.
3	50	25	1 : 3	20 to 30	25	None	74.0	67.3			Dark-red product; odor of toluene.
4	50	25	1 : 3	25 to 55	20	2 hours up to 94° C.[a]					Black mixture; no separation.
5	50	40	1 : 2	25 to 50	25	None	79.0	75.7	1.2194	11.17	
6	50	50	1 : 1.5	20 to 30	25	1 hour up to 70° C.; 1 hour at 70° to 85° C.; 3 hours at 85° to 90° C.	81.0				
7	50	50	1 : 1.5	20 to 30	40	A few minutes at 50° C	81.0				
8	50	50	1 : 2	25 to 30	40	2 hours up to 97° C.; 2 hours at 93° to 97° C.	82.0				
9	50	50	1 : 2	25 to 30	25	None	82.0	78.0		11.36	
10	50	50	1 : 2	25 to 55	25	do	81.0	78.2	1.2400		
11	50	100	1 : 2	20 to 30	45	4½ hours at 90° to 95° C	90.0				Product mainly solid dinitrotoluene.
12	50	50	1 : 2	25 to 30	40	½ hour up to 95° C.; ½ hour at 95° to 97° C	81.8				
13	100	50	1 : 2	22 to 49	35	None	165.1				
14	100	50	1 : 2	25 to 58	18	do	164.0				
15	100	50	1 : 2	25 to 50	53	do	163.0				
16	200	50	1 : 2	12 to 30	105	do	328.4				
17	200	50	1 : 2	15 to 36	110	do	328.0	[b]73.0			
18	200	50	1 : 2	9 to 30	80	do	320.0	[c]71.5	1.1818	10.58	Acid added to toluene.
19	200	50	1 : 2	13 to 30	120	do	331.4	[d]243.4	1.2450	12.14	

[a] Excess HNO_3 increased to 50 per cent.
[b] From 82 grams of crude product.
[c] From 80 grams of crude product.
[d] From 248.55 grams of crude product.

PREPARATION OF TRINITROTOLUENE FROM MONONITROTOLUENE.

The preparation of trinitrotoluene from the crude mononitrotoluene was accomplished in an apparatus similar to that used in the preparation of the MNT. The vessel in which the nitration was effected was a tall beaker without lip, which was 23 cm. high and had a diameter of 8 cm. The beaker was placed on a sand bath, which could be heated with a gas burner as desired. To serve as a cover for the beaker a Florence flask from which the bottom had been removed, and to which a second neck about 1 cm. in diameter had been sealed at a distance of about 3 cm. from the original neck and parallel to it, was placed so as to fit closely on the flange of the beaker, the necks extending downward for about 6 cm. into the beaker. Through the smaller neck a thermometer was inserted; the larger neck equidistant from the sides of the beaker carried the glass stirrer and served as the opening through which the acids were dropped from a separatory funnel. The temperature of nitration was controlled by varying the rate at which the nitrating acid was added and by raising or lowering the flame.

At the completion of each operation the reaction products were allowed to cool to about 100° C., when they were transferred to a specially constructed separatory funnel by means of which a hot separation of the liquid nitration product was made; or, as was the general procedure, the contents of the funnel were allowed to stand about 18 hours, during which time the supernatant liquid TNT would solidify as a hard cake, and the dissolved TNT would crystallize out beneath. The spent acid was drained off from below. The solid cake of TNT from either procedure was crushed, combined with the remainder of the solid separated, and washed well with cold water. Afterwards this was repeatedly washed in the molten condition with hot water until free from acid. When the spent acids were poured into approximately 5 to 10 volumes of ice water and ice a second lot of crude TNT was obtained and treated in the same way. The crude products were then dried either over sulphuric acid in a vacuum desiccator or in an electric oven at a temperature of 50° to 60° C.

If further purification of the crude TNT thus obtained was desired, this was accomplished by crystallization from a mixture of 9 parts of 95 per cent alcohol and 1 part of benzene, or by the simpler operation of shaking the finely powdered solid for a short time with a cold mixture of the composition mentioned.

FOUR SERIES OF EXPERIMENTS.

Four series of experiments covering the preparation of TNT from MNT were performed as outlined below.

SERIES 1.

In series 1 the mononitrotoluene was dissolved in 100 per cent sulphuric acid and nitrated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and of 100 per cent sulphuric acid. The MNT used in each experiment was the total product obtained from the previous treatment of 50 grams of toluene. As 50 grams of pure toluene yields theoretically 74.46 grams of MNT, the latter figure was assumed to be the weight of the MNT in the crude product in calculating the amounts of nitric acid to be used in each experiment. To convert 74.46 grams of MNT into TNT requires theoretically 64.48 grams of anhydrous nitric acid or 72.78 grams of 94.09 per cent nitric acid having a specific gravity of 1.5.

SERIES 2.

In the experiments of series 2, with the exceptions noted in Table 2, following, the mononitrotoluene was dissolved in sulphuric acid having a specific gravity of 1.84, and was nitrated with a mixture of equal parts by weight of nitric acid having a specific gravity of 1.5 and of 100 per cent sulphuric acid.

SERIES 3.

In the experiments of series 3 the nitration of MNT may be considered as having been performed in two stages, but without a separation of the dinitrotoluene formed in the first stage of the nitration.

Except in one experiment, the MNT dissolved in sulphuric acid of specific gravity 1.84 was first treated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and of sulphuric acid of specific gravity 1.84.

At the end of this stage in the nitration 15 per cent oleum was added to the reaction mixture to concentrate the acids, after which the nitration was completed with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and of 15 per cent oleum.

SERIES 4.

In the experiments of series 4 trinitrotoluene was prepared from mononitrotoluene in two distinct steps involving the actual separation of the DNT formed in the first stage of nitration. The experiments were made for the purpose of comparing the results with those of the experiments in series 3.

TABULATION OF RESULTS.

Table 2 following gives detailed results of the experiments.

TABLE 2.—*Results of experiments on the preparation of trinitrotoluene from mononitrotoluene.*

SERIES 1.

Experiment No.	Mononitrotoluene.				Acid mixture added.				Period of addition of acid mixture.	Temperature during addition of acid mixture.			Subsequent heating.			
	Quantity of crude product.	Crude product derived from experiment No. —.[a]	Quantity of sulphuric acid used to dissolve crude product.	Strength of acid, per cent H_2SO_4	Nitric acid, specific gravity 1.5.		Sulphuric acid.			Initial.	Maximum.	Final.	Period.	Initial.	Maximum.	Final.
					Quantity.	Excess.	Quantity.	Strength of acid, per cent H_2SO_4.								
	Grams.		*Grams.*		*Grams.*	*P. cent.*	*Grams.*		*Minutes.*	° *C.*	° *C.*	° *C.*	*Minutes.*	° *C.*	° *C.*	° *C.*
.....	81.80	12	218.34	100.0	109.17	50	109.17	100.0	50	60	164	115	60	115	130	120
													60	120	150	145
													60	145	160	155
2.....	82.00	14	291.12	100.0	145.56	100	145.56	100.0	45	50	155	130	60	130	120	130
													60	130	140	140
													60	140	160	150
3.....	90.00	11	291.12	100.0	145.56	100	145.56	100.0	60	50	140	108	60	60	130	130
													105	130	150	150

SERIES 2.

1.....	82.50	13	218.34	95.6	109.17	50	109.17	100.0	30	50	139	95	35	95	136	120
													35	120	130	130
2.....	82.50	13	218.34	95.6	109.17	50	109.17	100.0	27	50	118	103	120	120	130	130
													60	130	150	125
3.....	82.00	16	291.12	95.6	145.56	100	145.56	100.0	75	50	144	130	60	130	150	150
4.....	82.00	17	291.12	95.6	145.56	100	145.56	100.0	120	24	135	135	60	135	140	140
													60	140	150	150
													60	150	160	160
													60	120	130	130
5.....	82.00	14	291.12	95.6	145.56	100	145.56	100.0	60	50	138	120	30	130	140	140
													60	140	150	150
													30	150	155	155
													120	110	125	125
6.....	82.00	16	436.68	95.6	218.34	200	218.34	100.0	50	50	122	104	60	125	140	140
													30	140	150	150
7.....	81.50	15	.....	.....	[b] 145.56	100	[b] 291.12	95.6	60	80	150	150	30	150	150	140
							145.56	100.0					30	140	155	[c] 155
													30	110	120	120
8.....	81.50	15	193.64	95.6	218.34	200	170.26	100.0	70	30	110	105	30	120	140	140
													30	140	150	150
													30	150	150	125
9.....	82.00	16	291.12	95.6	145.56	100	145.56	95.6	60	50	133	127	75	127	140	140
													30	140	150	150

SERIES 3.

1	A	82.00	16	145.56	95.6	72.78	*d* 100	72.78	100.0	40	50	113	95				
	B *e*					72.78	*f* 100	72.78	15% oleum	60	71	150	130	60	130	150	150
														60	150	150	120
2	A	82.00	17	109.16	95.6	54.58	*d* 50	54.58	95.6	45	50	105	75	10	95	120	120
														30	120	135	110
	B *g*					72.78	*f* 100	72.78	15% oleum	50	98	138	133	60	133	138	138
														60	138	138	130
														60	130	150	150
														30	150	150	140
3	A	80.00	18	109.16	95.6	54.58	*d* 50	54.58	95.6	45	50	115	70	40	70	124	124
	B *h*					72.78	*f* 100	72.78	15% oleum	35	100	151	132	60	132	139	121
														60	121	136	136
														60	136	139	139
														60	139	150	140
4	A	80.00	18	109.16	95.6	54.58	*d* 50	54.58	95.6	60	50	98	95	60	95	109	100
														60	100	100	83
	B *i*					72.78	*f* 100	72.78	15% oleum	30	80	115	115				
										30	115	115	84	120	100	117	117
										60	84	100	100				
5	A	82.85	19	109.16	95.6	54.58	*d* 50	54.58	95.6	60	50	100	100	60	100	107	107
														60	107	107	91
	B *j*					72.78	*f* 100	72.78	15% oleum	30	84	100	100				
										30	100	106	106	60	93	94	94
										60	106	106	93	60	94	117	95

SERIES 4.

1	A	82.00	17	109.16	95.6	54.58	*d* 50	54.58	95.6	70	60	113	113	120	113	119	108
														60	108	117	117
														60	117	117	100
	B *k*					72.78	*f* 100	72.78	100.0	60	100	143	130	60	130	146	136
														60	136	136	131
														60	131	135	135
														60	135	148	148
2	A	80.00	18	109.16	95.6	54.58	*d* 50	54.58	95.6	75	70	98	92	50	92	103	103
														60	67	67	43
	B *l*					72.78	*f* 100	72.78	15% oleum	80	35	70	67	60	43	75	65
														60	65	85	85
														60	85	101	101

See page 25 for footnotes.

TABLE 2.—*Results of experiments on the preparation of trinitrotoluene from mononitrotoluene*—Continued.

SERIES 1.

Experiment No.	Approximate water content of acids in reaction mixture (calculated).				Yield of trinitrotoluene.									
					Water-washed.			Washed with or crystallized from alcohol-benzene mixture.[m]				Crude product recovered from alcohol-benzene filtrate.		
	At beginning of nitration.	At end of first stage.	At beginning of second stage.	At end of second stage.	Quantity.	Per cent of theoretical.	Melting interval.	Quantity.	Per cent of theoretical.	Melting interval.	Nitrogen content.	Quantity.	Character.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Grams.*		° *C.*	*Grams.*		° *C.*	*Per cent.*	*Grams.*		
1	0.00	3.72	3.72	5.96	90.0	72.96	.....	*72.0	58.37	80 to 80.3	.....	20.0	Reddish-brown solid and liquid.	
2	.00	3.15	3.15	4.83	87.0 6.1	75.48	75 to 79 Less than 75	*69.0 * 5.0	60.00	80 to 81 73 to 80	.....	4.0	Solid and liquid mixture.	
3	.00	3.15	3.15	4.83	.....	.....	.....	*82.0	66.48	79.5 to 81	.....	11.0	Solid and liquid.	

SERIES 2.

1	4.40	5.91	5.91	8.15	100.0	81.07	46 to 66	*58.0	47.02	77 to 81	.....	34.0	Mixed solid and liquid.	
2	4.40	5.91	5.91	8.15	98.0	79.45	60 to 75	*69.0	55.94	80.2 to 80.6	.....	25.0	Red solid and liquid.	
3	4.40	5.35	5.35	7.03	90.0 5.5	77.42	67 to 79 Less than 60	78.0 3.0	65.67	80 to 81 57 to 77	.....	.....		
4	4.40	5.35	5.35	7.03	96.0	77.83	72 to 79	86.0 4.5	73.37	80 to 80.8 76 to 79	.....	.....		
5	4.40	5.35	5.35	7.03	97.5	79.04	[n]76 to 80	[o]*82.0 *6.0	71.34	80.3 to 81.3 78 to 79	(*p*)	6.0	Heavy red liquid.	
6	4.40	4.79	4.79	5.91	94.0	76.26	76 to 80	89.0	72.14	79.5 to 81	.....	.....		
7	3.67	5.35	5.35	7.03	94.0	76.26	68.5 to 78.5	82.0	66.48	79.5 to 81	.....	.....		
8	4.40	5.37	5.37	7.03	92.0 4.0	77.83	73 to 80.5	80.8 3.6	68.42	80 to 81 78 to 79	.....	.....		
9	4.40	6.45	6.45	8.13	94.5	76.61	50 to 73	73.0	59.18	79 to 81	.....	.....		

SERIES 3.

1	A B [e]	4.40	7.03	3.56	4.66	87.0 8.0	77.02	76 to 79.5 75 to 78	90.0	72.96	79.5 to 80.5	18.29	2.5	Dark brown mass.
2	A B [g]	4.40	9.25	4.20	5.28	92.0 4.5	78.23	74 to 80 74 to 77	90.0	72.96	79 to 81	18.41	2.5	Melting interval 74.5° to 78.5° C.

3	A	4.40	9.25	4.20	5.28	91.8	77.91	72 to 79	87.0	70.53	78.5 to 81.5			
	B [a]					4.3		67 to 77						
4	A	4.40	9.25	4.20	5.28	(q)	82.20		93.5	75.80	79 to 80.5	18.31	2.5	Melting interval 73° to 78° C.
	B [i]													
5	A	4.40	9.25	4.20	5.28	92.2	83.34	78 to 80	85.2	76.53	79 to 81	(r)		
	B [j]					10.6		69 to 75	9.2		78 to 81			

SERIES 4.

1	A	4.40	9.25	0.00	4.00	87.5	74.75	60 to 76	68.0	55.13	79.5 to 80.5			
	B [k]					4.7								
2	A	4.40	9.25	.00	2.30	[l]95.0	81.07	72 to 79.5	[l]87.0	74.18	79.5 to 81			
	B [f]													

[a] See Table 1, p. 19.

[b] MNT was added to the mixed acids.

[c] At this point the odor of MNT in the mixture showed incomplete action. After the addition of 100 per cent more nitric acid in excess the heating was continued two hours at a temperature of 115° to 135° C.

[d] In excess of that theoretically required to convert all the MNT into DNT.

[e] The reaction mixture of stage A was concentrated by the slow addition, during a period of 10 minutes (temperature, 65° to 71° C.), of 145.56 grams of 15 per cent oleum (fuming sulphuric acid containing 15 per cent free sulphur trioxide). The nitration was then continued by the use of an acid mixture containing 72.78 grams of nitric acid (100 per cent excess), having a specific gravity of 1.5 and an equal weight of 15 per cent oleum.

[f] In excess of that theoretically required to convert products of stage A into TNT (DNT into TNT).

[g] The reaction mixture of stage A was concentrated by the addition of 145.56 grams of 15 per cent oleum during a period of 15 minutes at a temperature of 105° to 97° C. Nitration was then continued with a mixture of 72.78 grams of nitric acid (100 per cent excess), having a specific gravity of 1.5, and an equal weight of 15 per cent oleum.

[h] The reaction mixture of stage A was concentrated and further nitrated as in 2B except that the time of adding the 145.56 grams of oleum was 25 minutes and the temperature was 110° to 100° C.

[i] The reaction mixture of stage A was concentrated and further nitrated as in 2B except that the time of adding the 145.56 grams of oleum was 20 minutes and the temperature was 83° to 80° C.

[j] The reaction mixture of stage A was concentrated and further nitrated as in 2B except that the time of adding the 145.56 grams of oleum was 40 minutes and the temperature range was 83°, 90°, 84° C.

[k] The total DNT product of stage A was dissolved in a mixture of 72.78 grams of 100 per cent sulphuric acid and an equal weight of 15 per cent oleum, further nitration being as indicated.

[l] The molten DNT of stage A was separated hot and treated with 145.56 grams of 15 per cent oleum during a period of 30 minutes, the temperature range being 78°, 150°, 35° C. In this experiment the spent acid separated from the molten DNT yielded approximately 4 grams of DNT, which was not included in the DNT nitrated to TNT. Theoretically this 4 grams should have yielded an additional 5 grams of water-washed TNT or 4.5 grams of purified TNT. The corrected yield of TNT should then be: Water-washed, 100 grams, washed with alcohol-benzene mixture, 91.5 grams, melting at 79.5° to 81° C.

[m] Values preceded by an asterisk (*) represent products obtained from water-washed product by crystallizing from alcohol-benzene mixture. All other values represent products obtained by simply washing water-washed products with alcohol-benzene mixture.

[n] In melting-point determination a very slight contraction of the substance was observed at 62° C.

[o] Solidification temperature of a 20-gram part was 78.6° C.

[p] Nitrogen determination on 82-gram part gave 18.34 per cent (calculated for pure TNT, 18.50 per cent).

[q] Separated hot, 70.4 grams, melting at 72.5° to 78.5° C.; crystallized from acid, 24.6 grams, having a melting point of 77.5° to 80° C.; precipitated in water, 6.4 grams, having a melting interval of 72.5° to 78° C.

[r] Nitrogen in 92.2-gram part of water-washed product before washing with alcohol-benzene mixture, 18.32 per cent; solidification temperature of 20 grams of this part, 79.2° C.

DISCUSSION OF RESULTS.

In Table 2 the calculated values representing the approximate water content of the acids in the reaction mixtures at successive stages of nitration are necessarily based on the arbitrary assumptions that no trinitrotoluene was formed until all of the mononitrotoluene had been converted into dinitrotoluene and that in series 1 and 2 no trinitrotoluene was formed until all of the mixed acid had been added. Further in the calculations the water formed during the successive stages of nitration was assumed to be the theoretical quantity, and no account was taken of changes in amount of acids due to the consumption or loss of acid.

It will be noted that in the experiments of series 1 and 2 the yields of TNT were lower and the water-washed products were of poorer quality than those of series 3. This result was probably due, in series 1, to the fact that in the initial stage of nitration the acids were too concentrated, and, in series 2, the second stage of nitration was necessarily effected with acids that had become somewhat too dilute. These difficulties in connection with the concentration of acids were obviated by the procedure in series 3. In these experiments the first stage of the nitration, mononitrotoluene to dinitrotoluene, was performed with weaker acids, after which the reaction mixture was concentrated by the addition of oleum, and the nitration was completed with the use of stronger acids.

A mean excess of 75 per cent of nitric acid over that required theoretically for the conversion of the MNT into TNT appeared to be quite sufficient.

A factor of evident importance is the temperature of nitration, as the experiments of series 3 clearly showed. By far the best results were obtained in experiments 4 and 5, in which the yields of water-washed product were 82.20 and 83.34 per cent of the theoretical, and the yields of purified product were 75.80 and 76.53 per cent. In experiment 5, nearly 75 per cent of the theoretical yield melted between 78° and 80° C. without any treatment other than that of thorough washing with cold and with hot water. In experiments 4 and 5 the temperature of nitration did not exceed 117° C.

Table 2 includes also the results of the two experiments performed according to method 4. In those two experiments also it is apparent that the lower temperature of nitration was more favorable to quantity and quality of yield. But the two experiments failed to show any advantage in respect to yield over the results of experiments 4 and 5 of series 3.

SUMMARY.

The results obtained in the experiments herein reported, especially those in experiments 4 and 5 of series 3, lead to the conclusion that the following procedure will give the best results in the preparation of trinitrotoluene:

OUTLINE OF MOST FAVORABLE METHOD OF PREPARING TRINITROTOLUENE.

The acid used in the first stage of the nitration of the toluene should be a mixture of two parts by weight of sulphuric acid of specific gravity 1.84 and one part of nitric acid of specific gravity 1.42, the weight of nitric acid taken being 50 per cent in excess of that required theoretically for the conversion of all the toluene into mononitrotoluene. For 50 grams of toluene 73.38 grams of nitric acid is used.

To the mixed acid contained in the nitrating vessel provided with apparatus for cooling and stirring, and cooled to 20° C. or lower, the toluene is added gradually, with constant stirring, the rate of introducing the toluene and the cooling of the reacting mixture being so regulated that the temperature does not exceed 30° C. When approximately 70 per cent of the toluene has been added, the nitration becomes much slower and little cooling of the mixture is required. When the total amount of the toluene has been introduced and the temperature ceases to rise, the cold water surrounding the nitrating vessel is allowed to run out while the operation is continued about one-half hour longer. After the contents of the nitrating vessel have stood for some time, preferably over night, the spent acids are removed by gravity from the supernatant crude mononitrotoluene, which consists of a mixture of mononitrotoluenes and dinitrotoluenes.

PREPARATION OF TRINITROTOLUENE FROM MONONITROTOLUENE.

FIRST STAGE.

The mixed acid used in the first step in the conversion of the crude mononitrotoluene into trinitrotoluene consists of equal weights of sulphuric acid of specific gravity 1.84 and of nitric acid of specific gravity 1.5, the nitric acid content being 50 per cent in excess of that required theoretically to convert the calculated yield of mononitrotoluene into dinitrotoluene. For the product derived from 50 grams of toluene, 54.58 grams of nitric acid is taken.

The crude mononitrotoluene is dissolved in sulphuric acid having a specific gravity of 1.84, the weight of the acid being equal to the weight of mixed acid, and is heated to 50° C. The mixed acid is added gradually, with constant stirring, over a period of at least one hour, during which time the temperature should not exceed

100° C. After all the acid has been introduced, the mixture is heated for two hours at a temperature of 90° to 100° C.

SECOND STAGE.

At this point the acids in the nitrating vessel, cooled to about 90° C., are concentrated by the addition of 15 per cent oleum, equal in weight to the weight of the mixed acid to be used in completing the nitration. If the oleum is added slowly, little rise in temperature occurs.

The mixed acid used consists of equal weights of nitric acid (specific gravity, 1.5) and 15 per cent oleum, the nitric acid taken being double that required theoretically to convert into trinitrotoluene the nitration products calculated as dinitrotoluene. On the basis of 50 grams of toluene, 72.78 grams of nitric acid is used.

The mixed acid is added gradually, with continued stirring, while the temperature is allowed to rise up to but not above 115° C. When approximately 75 per cent of the acid has been introduced, heating is required to maintain the temperature above 100 C.° A minimum time of two hours should be allowed for the introduction of the acid. When the addition of acid has been completed, the heating is continued for two hours longer, a temperature of 90° to 117° C. being maintained, but the latter temperature should not be exceeded.

Upon the completion of the nitration the reaction mixture is allowed to cool in a vessel adapted to the subsequent removal of the spent acid. After standing at least 18 hours, the crude trinitrotoluene will have separated as a solid cake and suspended crystals. After the underlying spent acid has been drained off, the crude product is crushed, washed well with cold and hot water, dried, etc., as previously described. A higher degree of purity may be obtained by washing with the alcohol-benzene mixture.

The spent acid contains in solution additional trinitrotoluene as well as lower nitration products, which may be recovered by precipitation in water. In practice the spent acid is used over again after renewal by the addition of fresh acids.

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